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FEASIBILITY DEMONSTRATION FOR ELECTROPLATING ULTRA-THIN POLYIMIDE FILM

BY

B. SCHNEIER, T.V. BRASWELL
AND R.W. VAUGHAN

AUGUST 1978

FINAL REPORT FOR
JPL CONTRACT 954771

This work was performed for the Jet Propulsion Laboratory,
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TRW

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TRW
TECHNICAL SERVICES CORPORATION

FOREWORD

This document represents the final report of the work performed between 22 August 1977 and 1 June 1978 by TRW DSSG for California Institute of Technology, Jet Propulsion Laboratory, under Contract 954771, NAS 7-100 T/O RD-156 on a program entitled "Experimental Program to Demonstrate Feasibility for Electroplating Large Quantities of Ultra-Thin Polyimide Film." This program was conducted under the technical direction of Mr. Robert Holtze, JPL Project Manager. At TRW DSSG, Robert W. Vaughan was Program Manager and Bernard Schneier was the Principal Investigator, assisted by Troy V. Braswell. Technical consultation was provided by R. J. Jones and M. K. O'Rell (polymer chemistry), Harry J. McCracken and Kenneth Lui (electroplating technology).

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I. INTRODUCTION AND SUMMARY

1.1 INTRODUCTION

The objective of the program was to demonstrate the feasibility of manufacturing approximately 10^6 m^2 of ultra-thin [10.2 ± 5.1 microns (μ) (40 ± 20) $\times 10^{-6}$ in)] polyimide film. Goals of the program were to provide polyimide film which possesses the following features:

- Capable of being joined in order to fabricate an 800 m by 800 m square from starting material 0.5 to 1 m wide
- Capable of being metalized or otherwise coated on both sides with one surface optically smooth
- Capable of being reinforced for tear resistance (rip-stop) or localized point loading either through an integral scrim or webbing or by externally attached techniques
- Stable in space for long periods of time exposed to elevated temperatures (310°C) and radiation
- Sufficiently flexible and durable to be folded in a small area for subsequent deployment in the space environment
- Equivalent in chemical, physical and mechanical properties to those of commercially available polyimide films of the same gauge (*e.g.*, etched Kapton film).

The approaches used to demonstrate the feasibility of fabricating large quantities of the film were to:

- Fabricate samples of film using dip-tank facilities
- Develop a small bench type facility and produce representative quantities of the film
- Determine the effect of applicable process parameters on thickness, uniformity and speed of film deposition
- Evaluate new methods of fabricating both plain and metallized (one side only) films using various types of temporary substrates

- Determine manufacturing methods for scale-up and estimates of the costs associated with these methods, including process control, quality assurance, *etc.*
- Determine raw materials, facilities and equipment and an estimate of their costs that are capable of producing $\sim 10^6 \text{m}^2$ of the film by January 1979
- Determine costs of finished products.

1.2 TECHNICAL SUMMARY

1.2.1 Polyimide film, $10.2 \pm 5.1 \mu$ ($40 \pm 20 \times 10^{-6}$ in), can be obtained by electrodeposition through laboratory control of the variables, voltage, current and immersion time.

1.2.2 Ultra-thin polyimide film can be prepared as either a plain film or as a film metalized (aluminum) on one side. The conditions for obtaining a strippable film need further definition.

1.2.3 Ultra-thin polyimide exhibits tensile properties characteristic of those reported for commercially available film.

1.2.4 Photomicrographs illustrate that the surface of metalized ultra-thin polyimide film can be compared with that of a commercially available polyimide film of thicker gauge.

1.2.5 Results of infrared analysis indicate that cure of ultra-thin polyimide film can be effected at 149°C under vacuum. In this program, film was routinely cured 18 hrs at 186°C . Further studies are needed to optimize cure conditions at lower temperatures and to determine the correspondence between cure conditions and film properties.

1.2.6 Manufacture of ultra-thin polyimide film (conceptual) employs equipment and techniques used in the laminating (coating) industries.

II. TECHNICAL DISCUSSION

2.1 INTRODUCTION

An experimental program was conducted to demonstrate the feasibility of electroplating large quantities of ultra-thin polyimide (PI) film 10.2 ± 5.1 microns (μ) [$(40 \times 10^{-6} \text{ in} \pm 20 \times 10^{-6} \text{ in})$]. In these studies, a dilute polyimide solution was used as the bath; aluminum (as foil or as a vapor deposited coating) was immersed in an electrodeposition bath to determine the effect of electrodeposition variables on film thickness. The electrodeposited film was dried 2 hours at 93°C (primarily a solvent-removal step) and cured 18 hours at 186°C . The results of these studies showed that, from a conceptual viewpoint, satisfactory film metalized on one side can be obtained by electrodeposition of polyimide onto an aluminum substrate. Using mechanical properties as a basis for comparison the cured ultra-thin polyimide film exhibits properties equivalent to those of commercial film. In addition, the effect of handling procedures on the film surface appearance was examined. Using photomicrographs as criteria, the surface appearance of strippable ultra-thin polyimide film compares favorably with that of a sample of commercial film of thicker gauge. Finally, the feasibility of effecting a cure at lower temperatures was investigated. The results of infrared studies indicate that imide formation (curing) takes place at 149°C under vacuum.

The studies have identified several areas which require further attention.

2.2 ELECTRODEPOSITION STUDIES

2.2.1 Electroplating Solution and Equipment

Table 1 shows the composition of the electroplating solution. In order to make up the electroplating bath, Pyre-ML enamel, supplied as $17.0 \pm 0.5\%$ w/w in N-methyl-2-pyrrolidone, was added slowly with stirring and dissolved in dimethylsulfoxide (DMSO). Triethyl amine was then added slowly with stirring. The solution was heated to 40°C and held at this temperature for 15 minutes. The warm solution was added slowly and with vigorous stirring to acetone. The electroplating solution was stored at 23°C . Acetone was added prior to use to maintain the above concentration. Periodically, over a 4-month period, portions of the bath were removed to carry out various studies. There were no apparent electroplating bath problems.

Table 1. Composition of Electroplating Solution

Ingredient	Volume, ml
Pyre-ML RC-5057	200
Dimethylsulfoxide	800
Triethyl amine	40
Acetone	3780

For initial studies a dip tank was used to determine the effect of electrodeposition variables on film thickness. The results of these studies were promising and prompted the adaption of equipment to demonstrate on a laboratory scale the manufacturing (conceptual) feasibility for electroplating large quantities of ultra-thin polyimide film.

Figures 1 and 2 show the bench scale apparatus prior to the start of an experiment. The unit consisted of a drum, 16.8-cm diameter, attached to a variable speed motor and connected to the ground terminal of a regulated power supply. The second terminal was connected to an aluminum plate set on the bottom of a pyrex dish intended for the electrodeposition bath.

In practice, the polyimide film was electrodeposited on aluminum foil wrapped circumferentially about the drum. The deposition time was studied by varying the drum speed as it rotated in the bath. As shown, a laboratory jack was employed to control the level of immersion of the drum in the bath. In operation this was difficult to control. Consequently, efforts were made to examine several variables for each run.

Finally, attempts were made to measure the film thickness directly. Use of weighing techniques was considered unsatisfactory because the method provides an indirect value only. Several direct measuring instruments were tried and were inadequate for this program including Permascope Eddy Current Thickness Gauge, Dermatron Digital Eddy Current Unit, Micro-Derm Beta Backscatter Thickness Instrument, Infrared Reflectometer Inspection Device. Direct thickness measurements of the electrodeposited film thickness were successfully made using a profilometer. This instrument provided an autographic trace of a probe movement traversing the step from the film to the aluminum substrate.

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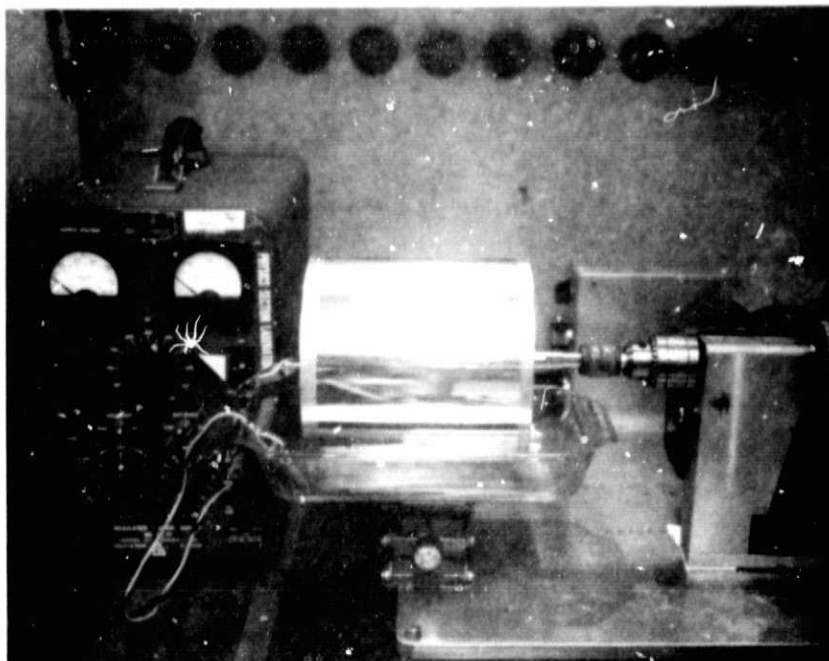


Figure 1. Electrodeposition Apparatus

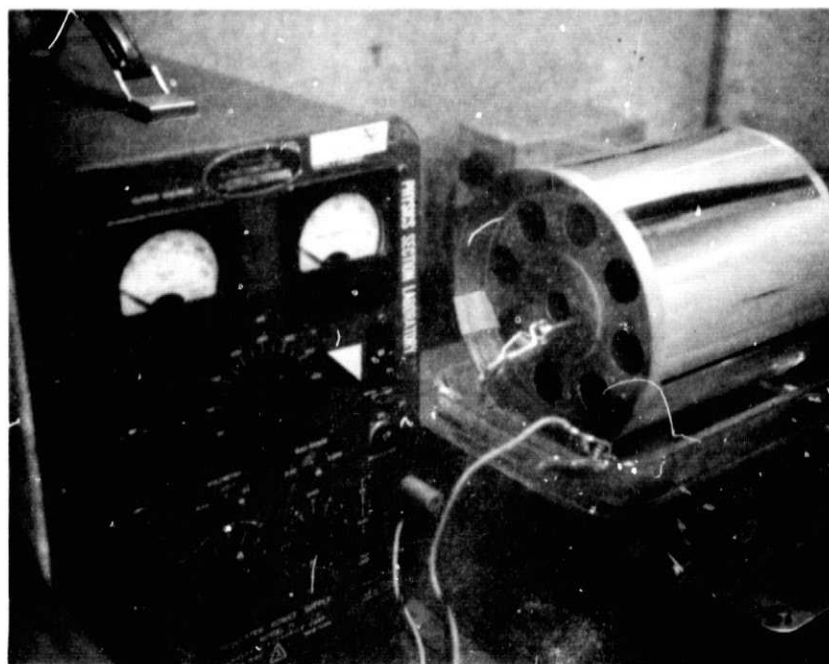


Figure 2. Bench Scale Apparatus

2.2.2 Electrodeposition Variables

Studies were conducted to determine the effect of electrodeposition variables on film thickness (voltage, current and the time the aluminum substrate is immersed in the electrodeposition bath). Preliminary data were obtained on aluminum foil immersed in a jar containing the electrodeposition bath. In these studies, power (voltage times current) was held constant and immersion time varied, 90 sec. and 15 sec. The results presented in Table 2 show that at constant power, as immersion time decreased, film thickness decreased from 129.5μ to 25.4μ . This value is greater than the program target range of 5.1μ to 15.3μ . Additional investigations were conducted using the bench scale apparatus.

Table 2. Effect of Immersion Time on Electrodeposited Film Thickness (Dip Tank Method)

Sample 12931-	Electrodeposition Conditions			Film Thickness* micron, μ
	Voltage Volts	Current Milliamps	Time, sec	
26-2	100	100	90	1295
26-3	100	100	15	254

*Target thickness: 5.1μ - 15.3μ (20×10^{-6} in - 60×10^{-6} in)

Table 3 presents data obtained with the bench scale apparatus. The effect of changes in the electrodeposition conditions on film thickness was studied anew. The preliminary results show that film thickness may be varied by altering the electrodeposition variables. In one series, immersion time was held constant at 6 sec. and power was changed (film was prepared in a single experiment). The results show that under these conditions a decrease in power was accompanied by a decrease in film thickness from 26.67μ to 1.27μ . It may be noted that one of the objectives of this program, the preparation of film in the range 5.1μ to 15.3μ thick, is encompassed in this series. The results obtained on sample 12931-26-6 show that a film thickness of 0.25μ was obtained if an immersion time of 1 sec. is used at a power value of 10000. Using a power value of 10000 as a basis for comparison, the data in Table 3 correlate well with those given in Table 2, a plot of film thickness vs immersion time shows that thickness

increases linearly with time. This agreement is considered satisfactory since the films were prepared by different immersion methods and the techniques are considered novel. Finally, based on these data, film of the required thickness can be obtained if the immersion time is about 4 to 10 seconds.

Table 3. Effect of Electrodeposition Conditions on Film Thickness (Bench Scale Apparatus)

Sample 12931-	Electrodeposition Conditions			Film Thickness* micron, μ
	Voltage Volts	Current Milliamps	Time sec	
26-4	30	135	15.2	30.48
25-5A	12.5	40	6	36.67
25-5B	6	25	6	6.35
25-5C	<1	12.5	6	1.27
26-6	50	200	1	0.25

* Target thickness: $5.1\mu - 15.3\mu$ (20×10^{-6} in - 60×10^{-6} in)

2.2.3 Etching Studies

Table 4 shows the results of studies carried out to determine the effect of acid strength on the rate of dissolution of the aluminum foil backing. In these studies, polyimide film was electrodeposited on foil 0.076 mm. thick, type 1145-H-19. Rectangular-shaped specimens, 6.4 cm. x 2.5 cm., were placed in containers containing HCl solutions. The time needed to dissolve the foil was noted. The results show that, at the acid levels tested, 6 N HCl appears more effective.

Table 4. Effect of Acid Strength on Rate of Dissolution of Aluminum Foil Backed with P.I. Film (Type 1145-H-19, 0.076 mm. thick)

HCl Conc.	Time*, Min.
0.12 N	180
1.2 N	>180
6.0 N	5
12.0 N	40

* 6.4 cm. x 2.5 cm. test pieces

As is well known, the mechanism of attack of metal by mineral acid proceeds with the evolution of hydrogen. For the case of aluminum, the reaction may be written as in Equation 1.



If the film is made in widths of one meter (a desirable aspect according to the plan) and assuming foil dimensions of one meter length and 0.076 mm thickness (0.003 in.), calculations provide 7.67 g-atoms as a value for the amount of aluminum metal contained in the foil. Using this as a figure of merit (according to equation 1) 11.50 moles of hydrogen gas would be evolved per square meter of manufactured PI film. Considering that the program was intended initially to demonstrate the feasibility of electroplating 10^6 m^2 of PI film, these calculations indicate that, if large scale manufacture involves an aluminum dissolution step, extreme precautions need to be taken to keep the concentration of hydrogen gas low, generally less than 4%. In addition, provisions need to be made for the handling of large amounts of acid. Finally, the surface of film obtained after the acid dissolution step is inferior to that of commercially available film. Based in part on these considerations, studies were conducted to determine if the aluminum acid dissolution step could be eliminated.

2.2.4 Strippable Film

Efforts were directed to preparing an ultra-thin PI film which could be stripped away from a substrate. In these studies intended to evaluate new methods of fabricating both plain and metalized film (one side only), glass and FEP were evaluated as substrates; coated aluminum also was tried. Polyvinyl alcohol was used as the coating agent since it could be conveniently washed away with water.

2.2.4.1 Plain Film

Studies were carried out to determine whether or not PI film could be electrodeposited on a substrate coated with polyvinyl alcohol (PVA). Initially, procedures to obtain satisfactory coatings were defined and polyvinyl alcohol (PVA), partially alcoholized grade, was assessed. Water solutions of PVA were prepared at 1% and 5% w/w solids. In order to obtain apparently satisfactory films (bubble-free), it was necessary to first filter the PVA solution and then remove entrapped air under vacuum; the coated plates were dried under vacuum at 70°C. Based on these procedures, and using PVA

solutions, alone and in combination with aluminum sulfate, aluminum and glass surfaces were successfully coated. Aluminum sulfate was incorporated for its possible enhancing effect on the electrodeposition process especially on nonmetallic surfaces. A second water soluble, film-forming polymer also was tried. The use of polyvinyl pyrrolidinone did not afford a continuous coating possibly because of poor wetting characteristics of the aluminum and glass substrates.

Initial studies were conducted to determine the effect of changes in the electrodeposition variables on film thickness. Preliminarily, results of previous studies, employing uncoated aluminum, were used as a basis for establishing conditions to be used in the current studies. For example, a film 6.35μ thick was obtained at a power factor of 150 and an immersion time of 6 seconds. It was expected that the presence of the PVA film would favor increased power and immersion time. Consequently, very high power factors (5000, 15000 and 37500) were used; immersion time was increased to 30 seconds. Using these harsh conditions, polyimide film was electrodeposited on the coated aluminum substrate; after drying, the film was stripped away from its aluminum backing. The film quality was not satisfactory since it was nonuniform, thicker than program requirements, and unevenly distributed on the aluminum substrate. Similar results were obtained when the coating consisted of PVA containing aluminum sulfate. However, the experiments were considered successful since the principle had been demonstrated that the electrodeposited film may be separated from the aluminum substrate indicating that the acid dissolution step may be eliminated.

Additional studies were carried out to prepare strippable film. In these experiments to electrodeposit polyimide onto an aluminum surface coated with PVA, power was held constant; voltage and current were varied. Table 5 presents the results of studies using coated and uncoated plates. When the specimens were removed from the plating solution the entire surface was uniformly covered by a liquid film as evidenced by its capability to refract light. After solvent removal, film electrodeposited on uncoated plates appeared uniform and without pinholes. When PVA coated plates were used as the substrate, portions of the very thin film appeared cloudy; it

Table 5. Effect of Electrodeposition Conditions on Film Quality

Sample 12931-26-	PVA Coating	Power Factor	Voltage Volts	Time, sec.	Film Quality
11	Yes	150	6	10	Cloudy areas
14	Yes	150	10	10	Cloudy areas
17a	No	250	10	10	Smooth, continuous
17b	No	150	6	30	Smooth, continuous

is quite likely that coverage was not complete. Like observations were made when the immersion time was reduced from 10 seconds to 8 and 5 seconds. Similarly, when the coating consisted of PVA containing aluminum sulfate, cloudy polyimide films were obtained. The results indicate that PVA films, alone and in combination with aluminum sulfate, interact with the ingredients of the plating solution (possibly DMSO and acetone). Attention then was turned to preparing a strippable metalized film.

2.2.4.2 Metalized Film (One Side Only)

As a basis for experiments to determine if metalized polyimide film (one side only) can be prepared, aluminum metal was vapor deposited on a PVA-coated aluminum substrate. In these studies, power was held constant at 150; immersion time was varied between 5 and 10 seconds. Solvent was removed from the electrodeposited film by heating at 93°C for 2 hours. Attempts to strip the film without tearing it were unsuccessful. Two approaches to stripping were tried. In one, the composite was heated to soften the PVA; the film did not release. Also, dissolution of the PVA film was tried. As expected, polymer solution was preceded by localized swelling of the PVA film. Tearing of the ultra-thin film was experienced and the operation could not easily be controlled.

Glass was evaluated as a substrate. Aluminum metal was vapor deposited on a glass surface coated with PVA. Stripping problems were experienced similar to those discussed above.

The use of FEP as a substrate presented a promising approach to a strippable ultra-thin PI film. Figure 3 shows a polyimide film partially stripped from an FEP surface; one face has an aluminum coating approximately 125 Å thick. In this study, the electrodeposited film was dried 2 hours at 93°C. In order to ensure the integrity of the metalized PI film during the stripping step, the film surface was coated with aqueous PVA solution (10%); the coating was dried about 1 hour at 93°C. After reinforcing the edges of the film with tape to reduce or prevent initiation of tearing during stripping, the film was stripped away from the FEP surface; the PVA film was washed away with water. Photomicrographs show that the surface of the ultra-thin PI film can be compared favorably with that of commercially available film, one mil thick.

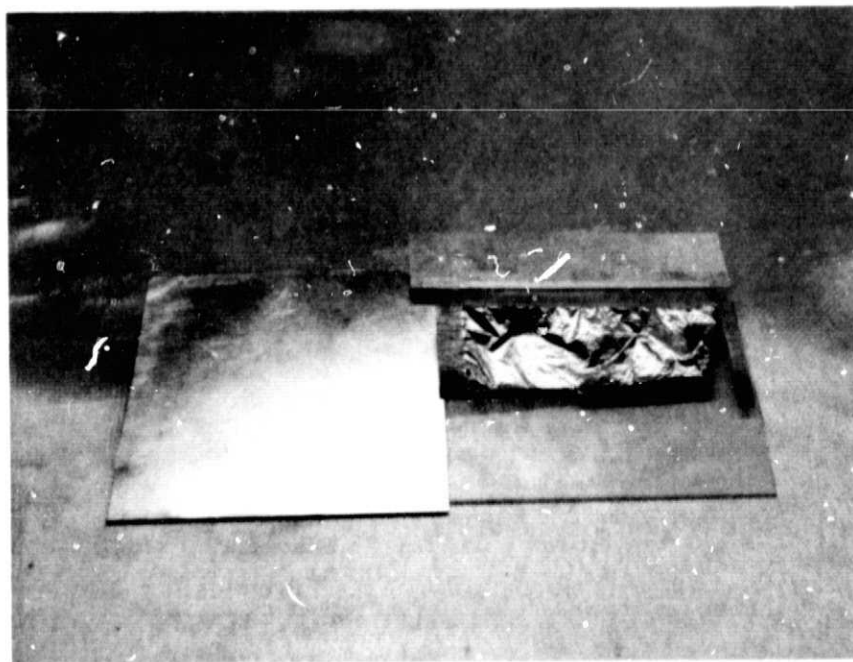


Figure 3. Strippable Metalized Polyimide Film

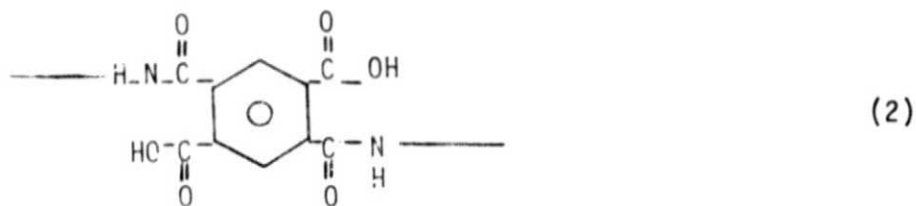
As noted, in a routine manner, aluminum was vapor deposited to a thickness of about 125 Å on various substrates. It was considered that if the thickness of the aluminum were increased approximately tenfold, the integrity of the electrodeposited PI film could more easily be maintained during the stripping operation.

Attempts were made to uniformly vapor deposit aluminum to a thickness of about 1000 Å on FEP film. The aluminum coated specimens were intended as substrates for studies to determine if the electrodeposited PI film can be adequately cured at lower temperatures - a second approach to ensure film integrity during stripping operations. Examination of the metal-coated sheeting revealed a large number of pinholes (about 46/cm², ranging in size from about 0.5 to 5 mils (cm.)). Prior to vapor deposition, TRW clean room cleaning procedures, among others, were employed to clean the FEP film (5 mil and 60 mil); glow discharge and ion bombardment techniques were also used. None of the procedures resulted in coatings free of pinholes when FEP was the substrate even though those deposited concurrently on glass contained no pinholes. Procedures for obtaining vapor deposited aluminum coatings on FEP substrates in thicknesses ranging from 500 Å to 1500 Å were considered to be outside the scope of the program and were not pursued further.

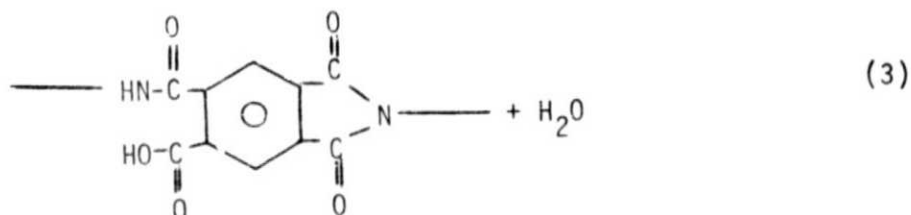
Cursory examination of the possible salutary contribution of the thicker aluminum coating to the stripping operation provided no concrete data. Electrodeposited PI film tore easily around the pinhole areas which were points of stress concentration.

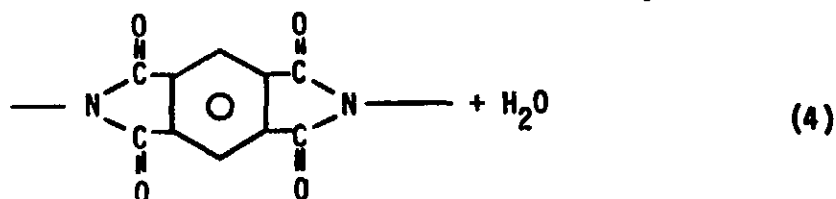
2.2.5 Cure Studies

The cure of ultra-thin polyimide film is generally considered to proceed in a stepwise manner. The "Pyre-ML" resin, reportedly based on pyromellitic dianhydride, may be depicted ideally as a substituted polyamic acid (Equation 2)



The film is probably electrodeposited on the aluminum substrate in this form. During the usual 18-hour period of exposure at 186°C, curing (ring closure) proceeds with the elimination of water, probably in a stepwise manner.





Studies were carried out to determine if the imide-forming ring closure step could be carried out at a lower temperature under vacuum. One of the purposes of the lower temperature cure was to reduce film distortion due to differences in thermal expansions of the various components of the composite. A second purpose was to reduce the exposure of the reflective aluminum surface to high temperatures. In these studies two cure schedules under vacuum were tried, 2 hours at 93°C and 18 hours at 149°C; vacuum, applied with the aid of a single stage pump, was estimated at 100 mm Hg. The films were submitted for infrared analysis.

The IR spectra of film cured under vacuum were compared to that obtained on film cured 18 hours at 186°C (sample 12931-26-4, Table 2). Based on these spectra, the results show that film cured 18 hours at 186°C was fully imidized. Film cured 2 hours under vacuum at 93°C existed mainly as the polyamic acid. Film cured under vacuum 18 hours at 149°C exhibits absorptions characteristic of the fully imidized polymer and also those of the polyamic acid. The results indicate that curing under vacuum at lower temperatures may be a viable method of curing ultra-thin polyimide film.

2.2.6 Film Properties

2.2.6.1 Tensile Strength

The tensile properties of the electrodeposited film 12931-26-4 (Table 2) were evaluated preliminarily. In these studies the film was dried 2 hours at 93°C; a portion was cured 18 hours at 186°C. (A postcure step, ordinarily 1 to 2 hours at 279°C, was not carried out.) Three specimens of each type were tested in tension at a rate of jaw separation of 13 cm./min. The results presented in Table 6 show that the reproducible tensile properties at 23°C obtained on the electrodeposited PI film are similar to those reported for commercially produced, postcured material.

Table 6. Tensile Strength of Electrodeposited PI Film

Sample 12931-26	Ultimate Tensile Strength, Psi		
	Obtained	Average	Reported ^(a)
4a (dried at 93°C)	31,166 33,333 35,167	33,200	15,000
4b (cured at 186°C)	23,767 24,233 23,867	23,600	

(a) Properties of Pyre ML, Dupont Bulletin No.25, June 1963.

2.2.6.2 Surface Appearance

To date, ultra-thin PI film has been prepared in the laboratory either metalized on one side or without the backing. In the latter case, the aluminum backing was dissolved in 6N hydrochloric acid; the film was subsequently washed and dried. In order to determine the adequacy of the PI film, standard SEM procedures were used to compare the surface of commercially-available Kapton film (.0025 cm thick) with that of ultra-thin PI film, plain and metalized on one surface.

Figure 4 shows that the Kapton film surface appears whole, uniform and characterized by cracks that are not connected but appear to run in one direction; possibly an indication of mandrel winding direction.

Figure 5 shows that the metalized ultra-thin PI film appears whole with little evidence of cracking except in those areas of wrinkled aluminum.

Figure 6 shows that the plain unsupported ultra-thin PI film exhibits a number of irregularly shaped holes. It is considered likely that the defects arise from impingement of partially dissolved aluminum particles on the film during the acid treat step. The microphotographs do illustrate that satisfactory quality, metalized ultra-thin PI film (one side only) can be obtained.

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Figure 4. SEM Photomicrograph of Commercially Available Kapton Film, .0025 cm thick

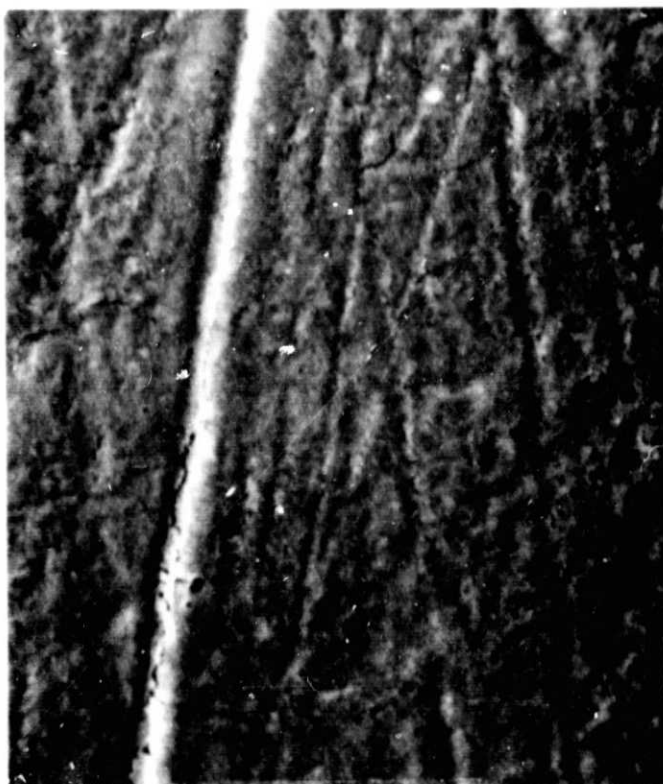


Figure 5. Ultra-Thin Polyimide Film With Aluminum Backing

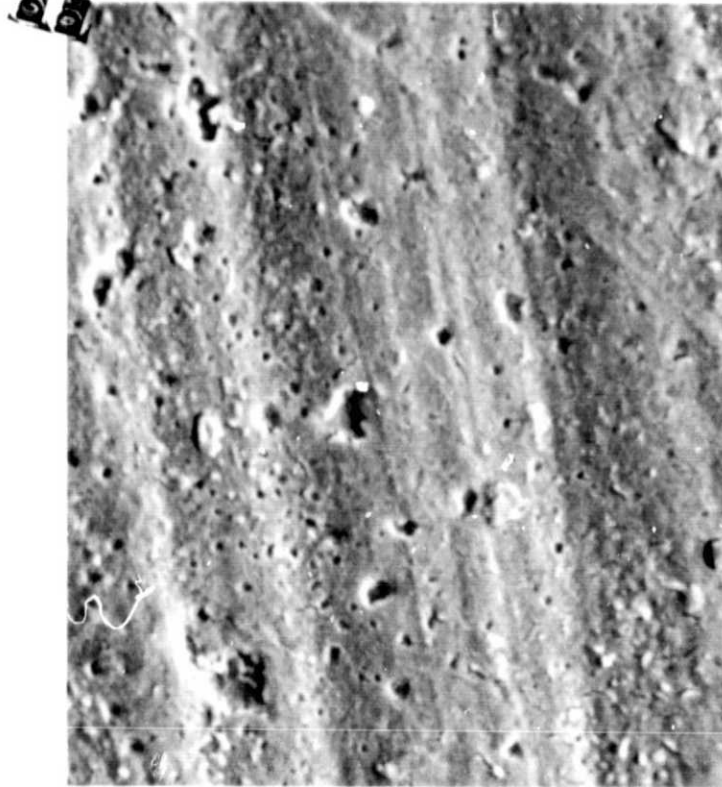


Figure 6. Unsupported Ultra-Thin PI Film

2.3 PROBLEM AREAS

The major problem encountered during the course of the feasibility program was difficulty in handling the electrodeposited film. Other problems arose and can be characterized as being outside the scope of the primary objective of the program. They include the unavailability of strippable, aluminum coated FEP film and difficulties in obtaining vapor deposited aluminum coatings in the range of $1000 \text{ \AA} \pm 500 \text{ \AA}$ thickness and without pinholes.

As noted, the studies with metalized film were conducted using coatings approximately $125 \text{ \AA}$. Aluminum coated FEP sheeting is commercially available in roll form from G. T. Schjeldahl Company, Northfield, Minnesota. A sample of the composite, 5 mils thick, was obtained. Various attempts to strip the aluminum from the FEP backing were unsuccessful even though the procedures were those used successfully previously. Further inquiries revealed the company claims it can supply strippable aluminum coated FEP sheeting.

One sample was evaluated. Polyimide film was electrodeposited onto the substrate. However, the metalized film could not be stripped away from the substrate. Pursuit of this subject is desirable because, if successful, the use of commercially available sheeting may provide the entrance to eliminating the need for the release (PVA) coating. It is evident that although a strippable film was obtained, the conditions leading to reproducible, release-type films need to be identified and clarified. Finally, depending on the mode and degree of adhesion between the aluminum and FEP substrate, the handling problem may be alleviated. If the aluminum backing is only lightly bonded mechanically and/or chemically to the FEP substrate, strippability may be enhanced.

The problem of the PI film handling manifested itself in a number of ways, including the cure step. In these studies, curing was effected of a composite comprising electrodeposited PI film/vapor deposited aluminum/PVA coating/substrate such as FEP sheeting. It should be recalled that during the initial, drying step at 93°C, principally, DMSO and acetone (electrodeposition bath solvents) are volatilized; polyimide exists primarily as its precursor, a chain-extended amic acid type. In this form, as with all materials, the film can expand under the application of heat although each component of the composite expands at a different rate. During the cure period at 186°C, ring closure (cyclization) with elimination of water occurs to form the polyimide; the chain-extended amic acid type material undergoes imidization. The differences in rates of thermal expansion of the various components (Table 7), exaggerated by the long exposure to 186°C, resulted in uneven, wavy film. It would be expected that film distortion could be reduced if the polyimide is cured at lower temperatures and the metalized film (metal side) is partially released from the FEP substrate.

Table 7. Linear Coefficient of Thermal Expansion

Polymer	Value/°C
Pyre-ML ^(a)	4.0×10^{-5}
FEP	8.3×10^{-5}
Aluminum (6061)	2.3×10^{-5}

(a) Properties of Pyre-ML, Dupont Bulletin 19.

Finally, film handling problems arise from the thinness of the film, either plain or metalized on one side. To prevent tearing, the film needs to be protected from environments such as air turbulence.

2.4 MANUFACTURE OF ULTRA-THIN POLYIMIDE FILM (CONCEPTIONALIZED)

2.4.1 Manufacture

The manufacture of ultra-thin polyimide film can be described as a process involving electrodeposition from solution onto a metal (aluminum) foil. The foil, in the form of a composite, is coated on one side with a thermally stable polymer which is weakly bonded to the base aluminum; the face of the foil is very smooth. Polyimide is electrodeposited onto the smooth surface; the polyimide side of the foil then becomes the outer ply of the laminate.

The manufacturing process can be divided into various steps. The Pyre-ML varnish is placed in a reservoir from which it can be fed to a shallow pan and then brought into contact with the aluminum face. A single immersion arrangement is needed in which the varnish contacts only the aluminum side. The resin pickup can be controlled by the immersion time in the electrodeposition bath, and power factor.

After electrodeposition, the wet polyimide laminate is fed continuously onto a conveyor belt that takes the material through a series of air-circulating ovens where the solvents (DMSO, acetone) are evaporated and recovered. Temperatures are controlled in the range of 93°C to dry the material.

The dried material may again be rolled for storage or transit to the curing area. In other cases it may be cut to size, layed on supports (or supported from the sides) and cured. (To ease handling problems, the dimensions of the foil composite may be such that the width of the foil section is less than that of the plastic substrate. The exposed edges of the plastic can be perforated and the perforations fitted onto sprockets on driven wheels inside the oven. The ultra-thin polyimide film would be transported in much the same manner that film is transported in a camera.) Curing may be effected under vacuum.

Depending on plant lay-out, the polyimide film can be stripped either after drying or curing.

2.4.2 Operations Control

In the electrodeposition and drying operations, it is important to control the amount of resin in the electrodeposition bath, the amount deposited onto the foil, and the degrees to which it is dried and cured.

- Pyre-ML controls

Initially, Dupont material specifications may be used as a basis for incoming raw material specifications.

- Electrodeposition Bath Materials

Processing studies need to be conducted to determine levels of controls needed for triethyl amine concentration and solvents' purity.

- Thickness of Resin Electrodeposited on Foil

Thickness of polyimide film is the critical property of the electrodeposited film. Thickness should be measured directly with the aid of an instrument such as a profilometer. In line process controls are desirable and may be based on tests such as increase in weight of the foil composite. The controls can be based on studies to delineate the correspondence between results of accelerated drying procedures and normal one.

- Cure of Polyimide Film

A correlation can be established between requirements of program's mission(s) and the properties of the cured film. Using the results of infrared analysis as a basis for cure, a correlation can be established between film properties (tensile, electrical, *etc.*) and, for example, carbonyl absorption.

Another measure of degree of cure is by extractables. It is probable that fully cured polyimide exhibits solution properties different from partially imidized material.

2.4.3 Costs

Modern equipment uses high speed impregnators and dryers incorporating electronic devices and controls to permit throughputs of about 30 m/min. Based on this criterion and three shifts/day, 23 days are needed to manufacture 10^6 square meters film. Subcontracting this small operation to a laminator equipped with the necessary high speed rollers would provide manufacture feasibility without outlay for expensive capital equipment.

Estimate of costs of polyimide manufacture (10^6 square meters film, solid density = 1.059 g/cm^3 , thickness = $.10.2\mu$) is based on the following:

- Raw Materials

- FEP sheeting, aluminized one side, per 1000 sq.cm. \$2.68
- Pyre-ML [RC 5057, 17% (w/w) solids], per gallon \$32.61
- Dimethyl sulfoxide, per gallon \$50.00
- Acetone, per gallon \$13.45
- Triethyl amine, per gallon \$61.77

- Raw Material Cost/square meter

- FEP sheeting, aluminized one side \$26.80
- Pyre-ML (101.6×10^{-6} cm. thick) 5.08

The results show that raw material costs are about \$32 per square meter if solvent is recovered completely. The data indicate that re-use of the FEP sheeting must be included in a process involving electrodeposition on an aluminum substrate. Discounting the one time cost of FEP sheeting and providing \$0.10/1000 sq. cm as cost for vapor deposition of a strippable aluminum coating, the cost of metallized polyimide film (one side only) including process may be projected at about \$15/square meter.

III. CONCLUSIONS AND RECOMMENDATIONS

Based upon the results stated in Section II, this feasibility study has demonstrated on a laboratory scale that ultra-thin polyimide film can be prepared using electrodeposition techniques. The film is capable of being metalized on one side. The film exhibits tensile properties representative of a fully cured polyimide. The surface of the ultra-thin polyimide film is similar to that of commercially available polyimide film of up to 10^3 times an increase in thickness. The laboratory procedures are amenable to scaleup employing techniques used in the laminating (coating) industries.

It is recommended that additional studies should be conducted to develop this novel technology. Among the technical areas that require further investigation are procedures for obtaining strippable film reproducibly. Suitable conditions to cure the ultra-thin polyimide at temperatures lower than 186°C to 279°C need to be defined. One approach worthy of consideration would be the preparation of foil coated on both sides with ultra-thin polyimide film in order to protect the aluminum surface.